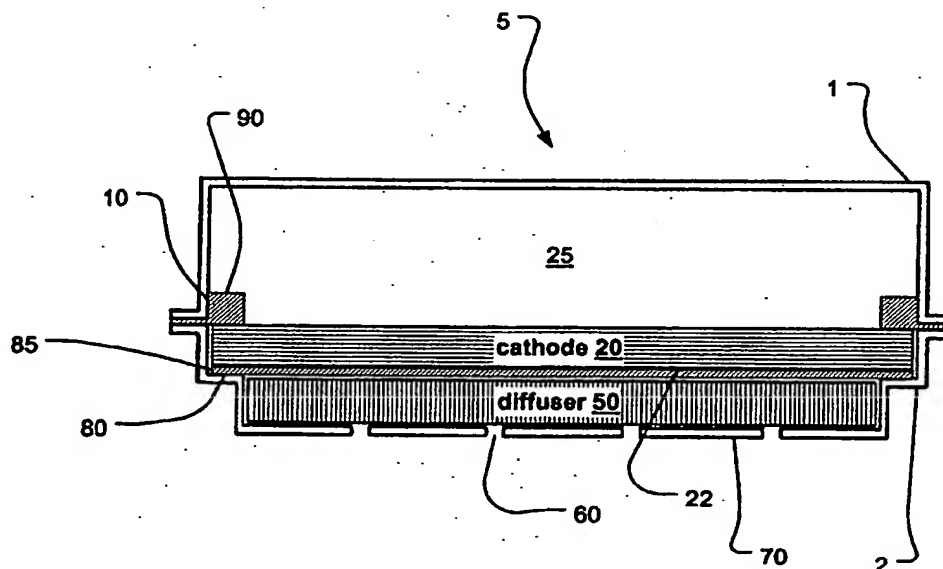




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(54) Title: AN AIR ELECTRODE PROVIDING HIGH CURRENT DENSITY FOR METAL-AIR BATTERIES



(57) Abstract

An air electrode for electrochemical cells provides high current capability over prior art cathodes. The electrode has an active layer of a carbon matrix with an oxygen reduction catalyst and a fluoropolymer binder. An embedded current collector is coated with a conductive material including a polymer binding agent and a conductive material, preferably of carbon. The active layer has a low density, preferably less than 1 g/cc. The electrode is a multilayer structure with a separator on one side of the active layer and a highly porous Teflon guard layer on the other side. The guard layer preferably has a porosity of at least 30 % and a thickness of no more than 100 microns. The surface of the active layer is roughened to facing the anode.

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An Air Electrode Providing High Current Density for Metal-Air Batteries

Cross Reference to Related Applications

Priority is claimed to the following United States Patent Applications: serial number
5 60/112,292, filed on December 15, 1998; serial number 09/286,563, filed on April 5, 1999
and 60/119,504, filed on February 10, 1999.

Background of the Invention

The present invention relates to electrochemical cells such as metal-air battery cells,
10 fuel cells, and the like. More particularly it relates to the air cathodes of such cells in
applications requiring high power output.

Secondary (rechargeable) batteries power most high-drain portable electronic
appliances. Examples of such high-drain devices are cellular telephones, notebook
computers, camcorders, and cordless hand-tools. The reason primary (disposable) batteries
15 are unattractive in such applications is that their service life is generally short, and the cost
and weight are high. For example, a cellular telephone, with alkaline batteries, would last
about as long as a single charge of a nickel-metal hydride battery. The cost per unit of energy
of alkaline batteries is very high and, consequently, they are unattractive for that purpose.
The low energy to weight ratio also makes them unattractive - a businessperson would have to
20 carry a substantial weight in primary batteries to remain self-sufficient on a long trip or flight.

New battery technologies have emerged that have, in principle at least, the ability to
offer much higher total stored energy at a low cost. Such technology would appear attractive
for high power, high-drain appliances. One such technology is zinc-air. In zinc-air batteries,
the cathode reduces ambient oxygen, which means that the battery has only a single
25 consumable electrode. This magnifies the energy capacity per given volume tremendously.
Unfortunately, this intrinsic benefit is attended by some troublesome requirements that make
zinc-air batteries unattractive.

One problem is the fact that, since air must enter the battery, water vapor can leave the
battery. Thus, zinc-air batteries are susceptible to dryout in low humidity environments,
30 potentially destroying their ability to function. The problem is exacerbated late in the
discharge/shelf-storage history of the cell by the decreasing moisture content of the cathode.

One prior art disclosure, USP 4,585,710, proposes an arrangement that reportedly prevents separator delamination and also helps prevent the air cathode from drying out. In this prior art disclosure, a gelling agent, such as a gelling agent commonly added to metal anodes, is applied between the cathode active layer and the separator layer to strengthen the adhesion
5 between the separator and the cathode.

Another problem is that zinc-air batteries, though having a high energy density, are typically low on power. In order for zinc-air batteries to generate more power, the reaction rate per unit area of the cathode must increase or the surface area of the cathode must increase. Increasing the area is difficult because of cost and mechanical design considerations, among
10 them, providing air access to a large surface area of the cathode for the diffusion of oxygen.

The cathode of a metal-air battery typically has an active layer of activated carbon, a catalyst, and a binder, which forms a network and holds the carbon together. Embedded within the active layer is a metal current collector. A guard layer covers the surface of the active layer that faces the outside air, and an ionically conducting separator covers the surface
15 that faces the anode. The guard layer keeps electrolyte from leaking out of the cell, and the separator separates the anode or an electrically conductive reaction product from the cathode active layer, thereby preventing an electrical short.

Polytetrafluoroethylene (PTFE) is an example of a suitable material for a binder, and manganese oxides and hydroxides are commonly used catalysts. A nickel screen is a
20 commonly used current collector although an expanded metal sheet or an alternative conductive material can be used, instead. The guard layer can be made of a sheet of porous PTFE, and the separator can be made of a semipermeable membrane or a porous material.

Another issue with regard to providing high current capacity is the various types of resistance in the battery. One solution that has been proposed by various parties is to provide
25 a polymer coating on the cathode current collector. The coating has a conductive filler, such as carbon. For example, US patents 5,447,809 and 5,814,419 discuss this idea. This approach has been discussed in the high current per unit area environment of cylindrical cells (D, C, A, AA, AAA cells used widely in consumer electronics and toys), in which the current collector is a smooth cylindrical surface. Since the surface area is so small in this type of cell and the
30 current demands typically so high, the smooth surface is a significant cause of resistance. But such coatings are not perfect. In cylindrical cells, the cathode current collector substrate is usually steel. In the '809 patent, the coating is described as being applied directly over steel.

This structure would invite corrosion and is unworkable for a practical battery. The 419 patent, which follows the '809 patent corrects this problem by proposing an additive in the coating or the steel substrate of silicic acid or sodium silicate, which, according the tests reported, improves performance. Also, at least one other reference discusses applying a
5 polymer coating over nickel to prevent corrosion.

Another approach to ameliorating the current collector-to-cathode resistance is a higher surface area of the current collector. For example, a number of battery designs have employed rippled casing surfaces or wire mesh screens as current collectors.

In the environment of cylindrical cells with smooth surface current collectors, polymer
10 coatings have been demonstrated to provide an advantage. However, in batteries with mesh-type current collectors such coatings have not previously been demonstrated to provide an advantage, and further, formulations have not been optimized. The chemistry and physics of air cathodes are not well understood and designing a cathode for a given level of power performance, manufacturability, durability, and other desired characteristics, in many ways, is
15 a very unpredictable proposition. Many different techniques must be used to address the different problems that limit performance. Experimental results in the various environments are crucial. The present invention results in a cathode that has a number of features that contribute to an improved performance within the constraints of this particular technical environment.

Objects and Summary of the Invention

The invention provides a cathode for electrochemical cells with numerous advantages including high current output, ease of manufacture, reliable cell construction, and longevity in dry environments.

25 Briefly, an air electrode for electrochemical cells provides high current capability over prior art cathodes. The electrode has an active layer of a carbon matrix with an oxygen reduction catalyst and a fluoropolymer binder. An embedded current collector is coated with a conductive material including a polymer binding agent and a conductive material, preferably of carbon. The active layer has a low density, preferably less than 1 g/cc. The electrode is
30 multilayer structure with a separator on one side of the active layer and a highly porous Teflon guard layer on the other side. The guard layer preferably has a porosity of at least 30% and a

thickness of no more than 100 microns. The surface of the active layer is roughened to facing the anode.

According to an embodiment, the invention provides an air cathode for an electrochemical cell. The cathode has an active layer, which may include carbon and an oxygen-reducing catalyst. The active layer may include a binding material such as a thermoplastic. Incorporated in the cathode is a metallic current collector in electrical contact with the active layer. The current collector is substantially covered in a conductive, non-metallic coating. The coating may contain, in substantial proportion, carbon in the form of graphite or carbon black. The coating may contain a non-conducting material combined with a conducting material, such that the coating forms a continuous hydrophobic layer. A thermoplastic used in the coating may be fluorinated ethylene propylene copolymer (FEP).

According to another embodiment, the invention provides an air cathode for an electrochemical cell. The cathode has an active layer, which may include carbon, a thermoplastic, and an oxygen-reducing catalyst. Incorporated in the cathode is a metallic current collector in electrical contact with the active layer. The current collector is substantially covered in a conductive, non-metallic coating, which contains a thermoplastic and carbon. The thermoplastic and the carbon may be present in substantially different proportions in the active layer as compared to the coating.

According to yet another embodiment, the invention provides an air cathode for an electrochemical cell. The cathode has an active layer, which may include carbon and an oxygen-reducing catalyst. Incorporated in the cathode is a metallic current collector in electrical contact with the active layer. The current collector is substantially covered in a conductive, non-metallic coating, which is bonded to the current collector. The coating may contain, in substantial proportion, a thermoplastic which bonds the coating to the current collector by sintering the thermoplastic to the current collector. The thermoplastic in this case also may be a fluoropolymer, such as FEP.

According to yet another embodiment, the invention provides an air cathode that has an active layer that includes a mixture of a divided mass of carbon, a divided mass of PTFE and a divided mass of a hydrophilic material. The hydrophilic material may be a cellulosic material, such as hydroxyethylcellulose.

According to yet another embodiment, the invention provides an air cathode for an electrochemical cell. The cathode has an active layer that includes a mixture of a divided

mass of carbon, a divided mass of thermoplastic and a divided mass of a hydrophilic material. The thermoplastic may be a fluoropolymer and the hydrophilic material may be a cellulosic material.

According to yet another embodiment, the invention provides an air cathode for an electrochemical cell with an active layer containing a substantial quantity of carbon and an oxygen-reducing catalyst. The cathode also has a separator sheet laminated to a primary surface of the active layer, which is effective to separate an anode from the active layer. The average pore size of the separator is between 0.25 and 2.0 microns. The separator can have an average pore size of at least 0.5 micron.

According to yet another embodiment, the invention provides an air cathode for an electrochemical cell. The active layer of the cathode includes a substantial quantity of carbon and an oxygen-reducing catalyst. The important feature is the average density of the active layer, which is not more than 1 g/cc. For better performance, the average density can be held to no more than 0.8 g/cc. The cathode can have a metallic current collector in electrical contact with the active layer with the current collector being substantially covered in a conductive, non-metallic coating. The coating may be bonded to the current collector. The coating may contain, in substantial proportion, a thermoplastic with the coating being bonded by a sintering of the thermoplastic to the current collector. The active layer and the coating may contain a thermoplastic in combination with carbon, with the thermoplastic and the carbon being present in substantially different proportions in the active layer as compared to the coating.

According to yet another embodiment, the invention provides an air cathode with an active layer containing at least an oxygen-reducing catalyst and carbon. The cathode has a current collector in electrical contact with the active layer and a conducting hydrophobic material bonded to a surface of the current collector. The conducting hydrophobic material may include a thermoplastic and the conducting hydrophobic material may be bonded to the current collector by the thermoplastic. At least a portion of the thermoplastic may be sintered to bond the coating to the current collector. The thermoplastic may be a fluoropolymer, e.g., FEP, and the hydrophobic material may include carbon. The active layer may have a surface that has a roughness of at least 10 micron pitch and depth to improve performance.

According to yet another embodiment, the invention provides a process for making an air cathode for an electrochemical cell. The method includes the step of forming an active

layer containing carbon, a binder, and an oxygen reducing catalyst so that at least one major surface of the active layer has a roughness of at least 10 micron pitch and depth.

According to yet another embodiment, the invention provides an air cathode for an electrochemical cell. The cathode in this embodiment has an active layer that contains a substantial quantity of carbon and an oxygen-reducing catalyst. There is a porous fluoropolymer sheet laminated to a surface of the active layer. The fluoropolymer sheet has an average porosity greater than 30% and a thickness of less than 100 microns. The porosity is preferably greater than 50%.

According to yet another embodiment, the invention provides an air cathode for a zinc-air battery. The active layer contains at least an oxygen-reducing catalyst and carbon. The cathode has a current collector in electrical contact with the active layer. The current collector has a conducting hydrophobic material bonded to a surface thereof. The conducting hydrophobic material preferably contains an insulating material that acts as a binder. The insulating material may be sinterable or thermally meltable, and the insulating material may be bonded to the surface of the current collector by sintering or melting the insulating material onto the current collector.

According to yet another embodiment, the invention provides an air cathode for an electrochemical cell, comprising an active layer that includes carbon, and an oxygen-reducing catalyst. The cathode has a current collector that is at least partly metallic with a conductive surface, whereby the current collector conducts electrical current from conductive material in contact with the surface. The current collector is substantially covered in a conductive, non-metallic coating bonded to the surface. The non-metallic coating is preferably bonded by means of a sintered thermoplastic, which forms a component of the composition of the coating.

According to yet another embodiment, the invention provides an air cathode for an electrochemical cell, comprising a laminated structure that includes an active layer. The active layer includes carbon and an oxygen-reducing catalyst. The cathode has a conductive current collector in electrical contact with the active layer, with the current collector being substantially coated in a conductive non-metallic coating. Preferably, the active layer includes a binding material. The binding material is, preferably, a thermoplastic. The coating may contain a non-conducting material combined with a conducting material, such that the coating forms a continuous hydrophobic layer. The non-conducting material may include a

thermoplastic which can be a fluoropolymer such as FEP. The active layer and the coating may contain a thermoplastic in combination with carbon with the thermoplastic and the carbon being present in substantially different proportions in the active layer as compared to the coating.

5 According to yet another embodiment, the invention provides an air cathode, which has an active layer made of carbon and an oxygen-reducing catalyst, and a metallic current collector in electrical contact with the active layer. The current collector is substantially covered in a conductive non-metallic coating containing a sinterable material that is bonded to the current collector by sintering. Preferably, the active layer has an average density of no
10 more than 1 g/cc.

The invention will be described in connection with certain preferred embodiments, with reference to the following illustrative figures so that it may be more fully understood.

With reference to the figures, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the
15 present invention only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of
20 the invention may be embodied in practice.

Brief Description of the Drawings

Fig. 1 is a schematic section view of a typical zinc-air battery cell that can make use of the air cathode of the present invention. The schematic is intended only to illustrate
25 relationships between various components.

Fig. 2 is schematic section, partial perspective, view of an air cathode illustrating some of the embodiments of the invention.

Description of the Invention

The invention provides an air-electrode for use in metal-air batteries, fuel cells, or any device that requires an air electrode, provides high current density, relative ease of manufacture, good humidity tolerance, and a number of other benefits.

5 The cathode described herein is intended for use in electrochemical cells or fuel cells. It is especially intended for use in primary metal-air battery cells, and especially zinc-air cells. The cells may be any suitable shape and be arranged in a housing that is liberally supplied with openings to allow air gases to be exchanged between the ambient air and the enclosed cells. The cells can have a housing of metal, plastic, or any other suitable material. Each cell
10 may have an array of air holes, such as used in zinc-air button cells, in such number and size as to allow oxygen to be supplied to a cathode inside the cell. The air holes of each cell may face either a plenum or the casing wall. The air holes are uniformly distributed, sized, and present in such number so as to insure that the cathode is not starved for oxygen, which could cause a drop in voltage. As an alternative to holes, the cell may use a semipermeable
15 membrane or structure that permits the diffusion of gases through the membrane or structure.

Referring to Fig. 1, each of the cells 5 contains at least one air cathode 20 and at least one zinc anode 25 with aqueous alkaline electrolyte (e.g., KOH). The cathode 20 lies adjacent a cathode side of the cell casing 2 and may be separated from that side by a diffuser 50. The diffuser 50 distributes oxygen from holes 60 in the cathode side of the cell 2 across the surface
20 of the cathode 20 and keeps the cathode 20 at a fixed distance, equal to the diffuser's 50 thickness, from the cathode side 2 of the cell 5. The diffuser 50 may be a porous material such as woven, knitted, or non-woven cloth or extended plastic mesh material. It may act as a standoff to prevent the air-side surface 22 of the cathode 20 from smothering any of the holes 60 when an expansion of the zinc anode 25 causes the surface to press against the inside wall
25 of the cathode side of the cell 2. The holes 60 in the cathode side of the cell 2 are uniformly distributed across the primary plane 70 of the cathode side of the cell.

The casing 1 / 2 of the cell may be formed in two halves, an anode side 1 and a cathode side 2 as in Fig. 1. The cell casing 1 / 2, may be formed of any suitable material. If the casing 1 / 2 is made of metal or any other conductive material, the two halves 1 and 2
30 should be insulated from one another. In either case, to form a primary seal 80, the cathode 20 may be attached to, or sealed against, the cathode side 2 of the cell casing 1 / 2. The primary

seal 80 may be effected by pressure, adhesive, or any other suitable means to prevent liquid electrolyte from leaking into the space occupied by the diffuser 50. That is, the primary seal 80 prevents liquid electrolyte from seeping around the cathode 20 into the area exposed to the outside air. A secondary seal 10 between the anode side of the cell 1 and the cathode side 2 prevents aqueous electrolyte from seeping around to the edge of the cathode 20 or leaking out of the cell 5. In the embodiment of Fig. 1, the secondary seal 10 is formed by a grommet 90, which also serves to insulate the anode side 1 and cathode side 2 of the cell casing 1 / 2 from each other. Pressure, an adhesive, or flowing sealant, or other suitable means may be used to effect the secondary seal 10.

Referring to Fig. 2, in an embodiment, the cathode consists of multiple layers with the middle layer being an active layer 120 composed primarily of carbon, PTFE, and a catalyst for reducing oxygen. Note that Fig. 2 is not to scale. The active layer 120 is the location where the oxygen reduction reaction takes place in the presence of the catalyst. A separator layer 100 which may be prelaminated to the active layer 120 can be made from microporous hydrophilic polypropylene (PP), polyethylene, PVC, cellophane, nylon, Celgard®, or other materials exhibiting similar properties. In some applications, the pore size of the separator 100 is in the range of about 0.25 micron to 2 microns instead of the more typical average pore size of less than 0.25 micron used in other battery applications. The larger pore size is sufficient to limit electrical shorts from crystallization of zinc oxide in the separator layer 100, and still permit enhanced wetting of the cathode active layer 120 with KOH solution. Other types of separator materials that may provide better cathode performance include microporous polyethylene or polypropylene whose hydrophilicities are enhanced by radiation grafting. Another class of suitable separator materials is semipermeable membranes based on cellophane, polyethylene, PVC, nylon, and polypropylene, for example, ZAMM-0 supplied by Pall RAI Corp. An additional non-woven, absorbent material can be added between the air electrode and the microporous separator or between the microporous separator and the zinc. The purpose of this is to provide an electrolyte reservoir.

The following processes may provide the preferred composition of the electrode active layer 120. The quantities are representative only and the quantities and proportions may be varied.

1. 240 g MnO_2 powder (Aldrich Chemical Company, Milwaukee, WI) is milled for 24 hours.
2. Add 2000 cc deionized water and heat to 85°C while stirring.
3. Slowly add 800 g activated carbon (Darco G-60 from American Norit, Atlanta GA).
4. Slowly add 288 cc PTFE suspension (grade 30-N from DuPont).
5. Continue stirring for an hour.
6. Filter and then dry at 120°C for about 5 hours.

10 An alternative process for making an active layer that starts with KMnO_4 instead of MnO_2 is described in US Patent 3,948,684, the entirety of which is incorporated herein by reference.

Embedded within the active layer 120 is a current collector 140 commonly formed of a metal, for example, a nickel, screen. Nickel-plated or nickel-clad steel, gold-plated metal, or other materials could also be used. A plastic element coated or clad with a conductor could even be used. It is preferred that the current collector 140 of the cathode be treated or constructed in such a way as to provide high surface area and low electrical resistance. The formation of oxide on the surface of a metal mesh current collector or a thin film of electrolyte on the hydrophilic surface of the current collector may limit the power capacity of the battery cell. One way to deal with this is to coat the current collector with a coating of a non-corroding metal finish. However, merely coating the current collector will not eliminate the disadvantages of remaining hydrophilic. Another option is to paint the electrode with a hydrophobic conductive paint. Hydrophobic conductive paints have other advantages over metal finishes. Gold and silver are the only metals that can be coated on a cathode mesh and still provide reasonable conductivity. Both are very expensive. Moreover, a silver coating is slightly soluble in alkaline electrolytes, which may lead to an increased corrosion of the zinc anode.

This paint may be applied before the cathode active layer is combined with the current collector. A preferred paint is a mixture of the following:

1. Fluorinated ethylene propylene copolymer (FEP) (Dupont 120-N or 121A) or some other thermoplastic, (e.g. polyolefin) preferably a fluoropolymer.

2. Isopropyl alcohol or some other suitable solvent (other alcohols, ketones, chlorinated hydrocarbons, etc.)
3. Acetylene carbon (Shawinigan carbon black made by Chevron) or some other suitable form of carbon, preferably hydrophobic, such as graphite.

5

A representative batch of paint may be formed of 1400 cc isopropyl alcohol, 108 cc FEP and 20 g acetylene black. The paint may be sprayed, or applied by any alternative suitable means, onto a mesh at a loading of 0.72 mg/cm^2 . This loading is only an example, and higher or lower loading values may also be used. The coated mesh is then baked in an oven at $290\text{--}330^\circ\text{C}$ to sinter the FEP and bond it to the metal current collector, e.g., woven nickel mesh. The actual sintering temperature, in applications of the present invention, may depend upon the particular thermoplastic used. Note that, in addition to sintering a sinterable material such as FEP, materials that can be melted to form a coherent mass could also be used in replacement of the sinterable material to bond the coating in place. The painted current collector may be heated by microwave, infrared, RF, or ultrasonic means instead of heating the coated mesh in an oven. The sintered coating forms a continuous hydrophobic conducting coating that protects against the corrosion or the oxidation of the metal mesh material. The sintering step also removes the surfactant in the FEP emulsion. It has been found that an air electrode with this coating laminated to a suitable separator and then incorporated into a zinc-air cell of area 10 cm^2 (2.5 cm. by 4 cm.) gave a steady state voltage 250 mV higher than an air electrode without this coating when discharged at a constant 0.47A.

To provide for high current capability in zinc-air batteries, the cathode should be fully saturated with electrolyte. The cathode tends to dry out as a result of water evaporating from the cell and as a result of waters of hydration being drawn away from the cathode when zinc oxide forms during discharge of the cell. The addition of hydrophilic agents to the cathode ameliorates this dryout effect. For example, cellulosic materials such as Natrosol® 250 MBR hydroxyethylcellulose (HEC) may be added to the cathode material (finely divided and added to the active layer mixture). As moisture leaves the cathode during discharge, the HEC holds onto this moisture and makes it available in the cathode despite the progressive drying of the cathode. A similar material has been used as a monolithic layer, but the incorporation of the material in its finely divided form inside the cathode active layer helps to insure that moisture

is held where it is needed. The following is an example construction of a cathode material using Natrosol.

240 g. of MnO_2 powder (Aldrich Chemical Company, Milwaukee, WI) is ground finely in a mill for 24 hours. The MnO_2 is then poured into 2 liters of deionized (DI) water and heated to 85°C . Add 800 g. of Darco G-60 carbon (American Norit, Atlanta GA) while stirring. Then add 288cc of Dupont 30-N PTFE suspension. Continue stirring for one hour, and then filter and dry at 120°C for 5 hours.

Slowly add 200g of the active mass made above to 5 liters of DI water stirred at 85°C . After all the carbon is in suspension, add 2 grams of Natrosol (grade 250MBR from Hercules). Continue stirring under heat until dry.

The active mass treated with the Natrosol® is spread evenly over a nickel mesh (40x40 mesh 0.005 mm dia. nickel from National Standard) and pressed to make an active layer of an air electrode. A porous PTFE sheet is then pressed on one side of the active layer.

The air electrode from above is then laminated with a microporous polypropylene film (grade 3501 from Celgard®) separator. The air electrode and separator laminate is then assembled into a zinc-air cell of area 10cm^2 containing 3.1g zinc and 2.4g 8M KOH solution, and the complete cell closed by crimping.

Testing Technique – The test cell and a control cell that does not contain the Natrosol® are exposed to a 25-30% relative humidity (RH) environment for a period of 7 days. After 7 days the cells are discharged under a load following a GSM profile, which is one of the standard profiles used by mobile communication devices for communicating with ground stations. GSM is a galvanostatic square wave profile consisting of 1.3A for 0.6 msec and 0.08A for 4.0 msec. The discharge cycle spans one hour (0.2Ah). The cells are then returned to the low humidity environment. This discharge cycle is repeated every 3-4 days until the cells fail. Failure is defined as the high current voltage falling below 0.9V.

Results - On the initial test after 7 days, both types of cells had a voltage above 0.9V. But when tested after a total of 11 days exposure to 25%RH, the cell without

Natrosol® failed. The cell with Natrosol® continued to work in similar tests over a period totaling 25 days in a 25%RH environment.

5 In Fig. 2, which shows a cross-section of the cathode, there is a guard layer 160, preferably formed of a PTFE film, laminated to the side of the active layer facing the air holes. The guard layer 160 allows oxygen to enter the cathode while preventing liquid electrolyte from leaking out. This layer 160 is preferably unsintered and highly porous to gases. The preferred porosity is at least 30%, but it is desirable to provide a guard layer that is even more porous. Porosity of 50% or more are even more preferable. The preferred
10 thickness of the guard layer is no more than 100 microns.

As visible in Fig. 1, an uncompressed PTFE film 85, which is separate from the laminated structure of the cathode 20, is uncompressed by any laminating process used to form the cathode structure shown in Fig. 2. During the manufacture of the cell, the grommet 90 forces the cathode 20 against the cathode side of the cell 2, thereby compressing the
15 previously uncompressed PTFE film 85. This helps to form the primary seal 80, which isolates the volume of the cell that is in communication with the outside air from the electrolyte as described above. Since the film 85 is initially uncompressed, it can act as a gasket to create or augment the secondary seal. Also, as discussed above, other means may be used to effect the seal 80 and the uncompressed PTFE layer 85 is not essential for this
20 purpose. The PTFE layers – the guard layer laminated to the cathode and the uncompressed layer – allow air to diffuse into the cathode while preventing liquid from leaking out.

In production, the active layer 120, the separator sheet 100, and the guard layer 160 may be laminated together to form a single structure. Representatively, the dimensions of the active layer and the separator layers are 0.20-0.50 mm and 0.025-0.25 mm, respectively. The
25 actual dimensions depend on the application and can be any suitable thickness. It is preferable that the final pressure used to laminate all the layers together not be too high.

It has been found that an active layer density of less than 1 g/cc is a suitable for attaining high current densities. It has been found that an active layer density of 0.8 g/cc is achievable and provides even greater current density potential. It was found that a PTFE layer
30 with a porosity greater than 50% and a thickness less than 100 microns and an active layer with a density less than 1 g/cc, and preferably less than 0.8 g/cc, exhibits a substantially

higher limiting current than prior art cathodes. Together, these improvements produce an air electrode with a limiting current greater than 400mA/cm^2 with a voltage greater than -300mV as compared to a Hg/HgO reference electrode at room temperature.

5 Still another feature that has been found to result in higher performance is a roughened surface on the cathode active layer facing the separator. Such a surface can be obtained by pressing the surface with an irregularly surfaced mold to form an imprint. Alternatively, various abrasion techniques, such as brushing, air blasting, or sandblasting; or various heat treatments, such as partial oxidation, can be used. The average roughness (R_a) of the surface, as measured by ANSI B46.1-1978, should be on the order of 10-100 microns instead of the
10 usual 0.1-1 microns.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative embodiments, and that the present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof. The present embodiments are therefore to be considered in all respects as illustrative
15 and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

Claims

We claim:

1. An air cathode for an electrochemical cell, comprising:
an active layer including a mixture of a divided mass of carbon, a divided mass of PTFE and a divided mass of a hydrophilic material.
2. A cathode as in claim 1, wherein said hydrophilic material is a cellulosic material.
3. A cathode as in claim 2, wherein said cellulosic material is hydroxyethylcellulose.
4. An air cathode for an electrochemical cell, comprising:
an active layer including a mixture of a divided mass of carbon, a divided mass of thermoplastic and a divided mass of a hydrophilic material.
5. A cathode as in claim 4, wherein said thermoplastic is a fluoropolymer.
6. A cathode as in claim 4, wherein said hydrophilic material is a cellulosic material.
7. An air cathode for an electrochemical cell, comprising:
an active layer containing a substantial quantity of carbon and an oxygen- reducing catalyst; and
a separator sheet laminated to a primary surface of said active layer effective to separate an anode from said active layer;
said separator having an average pore size of between 0.25 and 2.0 microns.
8. An air cathode as in claim 7, wherein said separator has an average pore size of at least 0.5 micron.
9. An air cathode for an electrochemical cell, comprising:
an active layer containing a substantial quantity of carbon and an oxygen- reducing catalyst;
an average density of said active layer being not more than 1 g/cc.
10. A cathode as in claim 9, wherein said average density is no more than 0.8 g/cc.
11. A cathode as in claim 9, further comprising:
a metallic current collector in electrical contact with said active layer;

3 said current collector being substantially covered in a conductive non-metallic coating.

1 12. A cathode as in claim 11, wherein said coating is bonded to said current
2 collector.

1 13. A cathode as in claim 11, wherein said coating contains, in substantial
2 proportion, a thermoplastic, said coating being bonded by a sintering of said thermoplastic.

1 14. A cathode as in claim 11, wherein:
2 said active layer contains carbon and a thermoplastic and said coating contains a
3 thermoplastic and carbon, said thermoplastic and said carbon being present in substantially
4 different proportions in said active layer as compared to said coating.

1 15. A cathode as in claim 9, wherein said active layer further includes a binding
2 material.

1 16. A cathode as in claim 15, wherein said binding material is a thermoplastic.

1 17. An air cathode for an electrochemical cell, comprising:
2 an active layer containing at least an oxygen-reducing catalyst and carbon;
3 a current collector in electrical contact with said active layer; and
4 a conducting hydrophobic material bonded to a surface of said current collector.

1 18. A cathode as in claim 17, wherein said conducting hydrophobic material includes
2 a thermoplastic and said conducting hydrophobic material is bonded to said current collector
3 by said thermoplastic, at least portions of which are sintered.

1 19. A cathode as in claim 18, wherein said thermoplastic is a fluoropolymer.

1 20. A cathode as in claim 18, wherein said conducting hydrophobic material includes
2 carbon.

1 21. A cathode as in claim 20, wherein said active layer has a surface that has a
2 roughness of at least 10 micron pitch and depth.

1 22. A cathode as in claim 17, wherein said active layer has a surface that has a
2 roughness of at least 10 micron pitch and depth.

1 23. A cathode as in claim 17, wherein said conducting hydrophobic material has a
2 continuous surface.

1 24. A cathode as in claim 23, wherein said hydrophobic material includes a
2 fluoropolymer.

1 25. A cathode as in claim 24, wherein said fluoropolymer is FEP.

1 26. A process for making an air cathode for an electrochemical cell, comprising the
2 steps of:

3 forming an active layer containing carbon, a binder, and an oxygen reducing catalyst;
4 said step of forming including forming at least one major surface of said active layer
5 with a roughness of at least 10 micron pitch and depth.

1 27. An air cathode for an electrochemical cell, comprising:
2 an active layer;

3 said active layer containing a substantial quantity of carbon and an oxygen-reducing
4 catalyst; and

5 a porous fluoropolymer sheet laminated to a surface of said active layer;
6 said fluoropolymer sheet having an average porosity greater than 30% and a thickness
7 of less than 100 microns.

1 28. A cathode as in claim 27, wherein said porosity is greater than 50%.

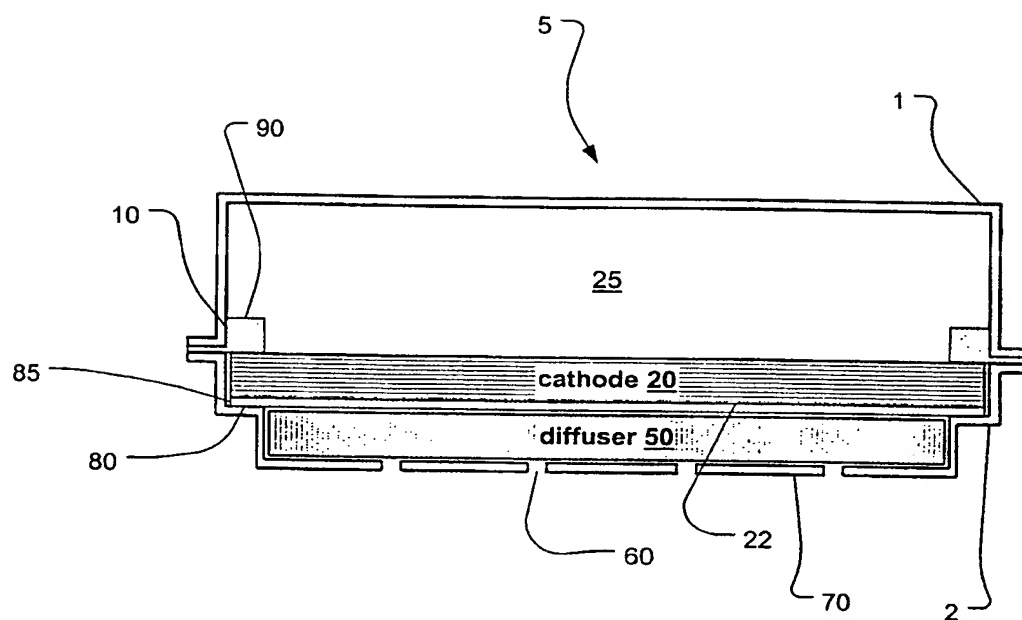
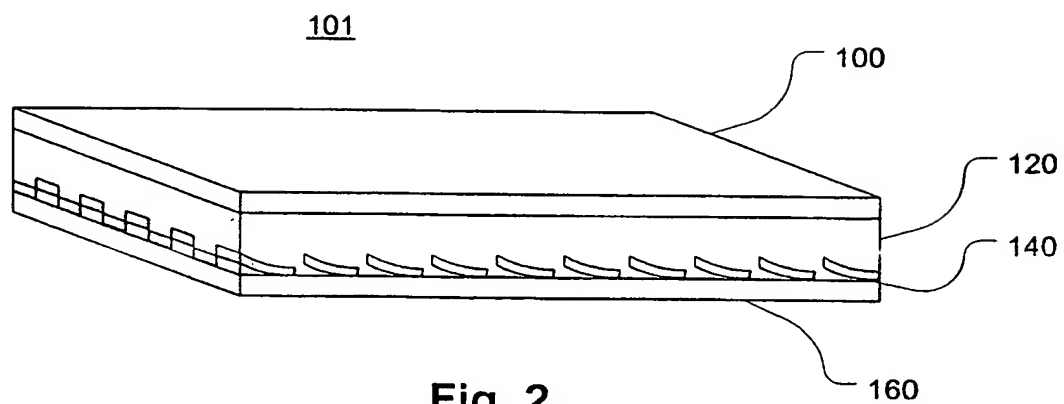


Fig. 1

2/2

**Fig. 2**

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/27996

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M4/62 H01M12/06 H01M8/22 H01M4/90 H01M4/96

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 298 690 A (ALCAN INT LTD., MONTREAL, CA) 11 January 1989 (1989-01-11) page 3, line 31 - page 4, line 15 page 5, line 7 - line 11 page 7, line 26 - line 31 figures 1,3	1,2,4-6
X	EP 0 580 278 A (ELECTRIC FUEL LTD., JERUSALEM, IL) 26 January 1994 (1994-01-26) page 7, line 22 - line 29 page 7, line 50 - line 55	1,4,5
A	---	26
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

7 March 2000

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INTERNATIONAL SEARCH REPORT

Int'l Application No
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C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 423 (C-638), 20 September 1989 (1989-09-20) & JP 01 160867 A (TORAY IND INC), 23 June 1989 (1989-06-23) abstract	3
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 272 (E-284), 13 December 1984 (1984-12-13) & JP 59 143276 A (MATSUSHITA DENKI SANGYO KK), 16 August 1984 (1984-08-16) abstract	7,9,11, 26,27
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 580 (E-1017), 25 December 1990 (1990-12-25) & JP 02 253573 A (TOSHIBA BATTERY CO LTD), 12 October 1990 (1990-10-12) abstract	7,8
A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 171 (C-291), 16 July 1985 (1985-07-16) & JP 60 044003 A (TOSHIBA KK), 8 March 1985 (1985-03-08) abstract	7,8
A	DATABASE WPI Section EI, Week 199515 Derwent Publications Ltd., London, GB; Class X16, AN 1995-111785 XP002132429 & JP 07 037584 A (EFL ELECTRIC FUEL LTD), 7 February 1995 (1995-02-07) abstract	9,10
Y	US 4 514 474 A (MOMYER WILLIAM R ET AL, PAOLO ALTO, US) 30 April 1985 (1985-04-30) column 1, line 53 - line 57 column 2, line 36 - column 3, line 19 figure 1	17,23
A		18,24
Y	PATENT ABSTRACTS OF JAPAN vol. 016, no. 513 (E-1283), 22 October 1992 (1992-10-22) & JP 04 192271 A (SEIKO EPSON CORP), 10 July 1992 (1992-07-10) abstract	17,23
A		24
	— —/—	

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/US 99/27996

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 1996, no. 12, 26 December 1996 (1996-12-26) & JP 08 203538 A (TOSHIBA BATTERY CO LTD), 9 August 1996 (1996-08-09) abstract</p>	27

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/27996

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0298690 A	11-01-1989	US 4885217 A AT 76538 T AU 610039 B CA 1307316 A CN 1031158 A,B DE 3871264 A JP 1033851 A MX 164273 B NO 883012 A,B, US 4906535 A US 5032473 A	05-12-1989 15-06-1992 09-05-1991 08-09-1992 15-02-1989 25-06-1992 03-02-1989 29-07-1992 09-01-1989 06-03-1990 16-07-1991
EP 0580278 A	26-01-1994	US 5242765 A AT 131959 T DE 69301073 D DE 69301073 T ES 2084450 T US 5312701 A	07-09-1993 15-01-1996 01-02-1996 04-07-1996 01-05-1996 17-05-1994
JP 01160867 A	23-06-1989	JP 2099319 C JP 8018882 B	22-10-1996 28-02-1996
JP 59143276 A	16-08-1984	JP 1968422 C JP 6101333 B	18-09-1995 12-12-1994
JP 02253573 A	12-10-1990	NONE	
JP 60044003 A	08-03-1985	NONE	
JP 7037584 A	07-02-1995	NONE	
US 4514474 A	30-04-1985	AU 549723 B AU 2652984 A BR 8406452 A CA 1212717 A EP 0140905 A ES 530477 D ES 538835 D IT 1179162 B JP 60500788 T MX 155313 A NO 844397 A WO 8403589 A	06-02-1986 28-09-1984 12-03-1985 14-10-1986 15-05-1985 16-06-1985 01-08-1986 16-09-1987 23-05-1985 16-02-1988 06-11-1984 13-09-1984
JP 04192271 A	10-07-1992	NONE	
JP 08203538 A	09-08-1996	NONE	

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